DESCRIPTION

5   EXHAUST GAS CLEANING-UP DEVICE

Technical Field

    This invention relates to a device for cleaning up exhaust gas from an engine.

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Background Art

    There is known a technique in which an absorbent comprising a zeolite (such as FER type zeolite, MOR type zeolite, FAU type zeolite, MFI type zeolite, β type zeolyte

15 or the like) is arranged in an exhaust passage of an engine so that HC contained in exhaust gas when the engine is cold-started is absorbed in the absorbent.

    However, generally, zeolite has a characteristic that it desorbs the absorbed HC as the temperature rises. From

20 a practical point of view, it is desirable that the desorption of HC from zeolite should start after a catalyst for converting and thereby removing HC (such as a three-way catalyst) warms to a temperature at which it acts properly and becomes activated.

25   In this connection, there has been developed an exhaust gas cleaning-up system in which various requirements are set on a zeolite of a type as mentioned above to optimize the HC absorbent (see Japanese Unexamined Patent Publication No. 2003-290661 and Japanese Unexamined

30 Patent Publication No. 2002-239346).

    The conventional HC absorbents using chiefly β type zeolite have, however, a problem that the desorption of HC from zeolite starts before a catalyst for converting and

thereby removing HC (such as a three-way catalyst) warms to a temperature at which it acts properly, so that the HC absorbed is not removed satisfactorily. A technique in which a metal such as Ag is arranged on a support with an
5   HC absorbent is effective to solve the problem of the HC desorption temperature. This technique has, however, a problem that it cannot provide a heat resistance sufficient for an exhaust gas cleaning-up device.

10   **Disclosure of the Invention**

This invention has been made to solve these problems. The primary object of this invention is to provide an exhaust gas cleaning-up device arranged such that HC can be held in an absorbent until a catalyst for converting and
15   thereby removing HC contained in exhaust gas reaches a temperature at which it acts properly.

In order to achieve this object, an exhaust gas cleaning-up device according to this invention comprises an absorbent comprising a zeolite having a three-dimensional
20   structure in which series of stacked rings consisting of a specific number of members intersect series of stacked rings consisting of a different specific number of members, said absorbent being arranged in an exhaust passage of an internal combustion engine. Hence, compared with the case
25   using conventional β type zeolite, it is possible to absorb a larger amount of HC in the absorbent catalyst and suppress the desorption of the absorbed HC, better.

It is desirable that the axes of stacked adjacent rings consisting of the same number of members should be
30   out of alignment. In that case, because of the structure of pores formed by the series of stacked rings, the desorption of the absorbed HC can be suppressed.

Further, it is desirable that the series of stacked

rings consisting of a specific number of members should have a function of absorbing HC contained in exhaust gas and the series of stacked rings consisting of a different specific number of members should have a function of

5   hindering the desorption of the absorbed HC. In that case, a large amount of HC can be absorbed and the desorption of HC can be suppressed up to a high temperature.

It is desirable that said specific numbers of members should be 10 and 12. In that case, HC can be easily

10   absorbed in the pores formed by the 12-membered rings, while the pores formed by the 10-membered rings can suppress the desorption of the absorbed HC.

It is desirable that the zeolite should have pores formed by the series of stacked 10-membered rings to extend

15   in the direction corresponding to one of the three dimensions of the three-dimensional structure and pores formed by the series of stacked 12-membered rings to extend in the directions corresponding to the other two dimensions of the three-dimensional structure. In that case, compared

20   with the case using conventional β type zeolite, the desorption of the absorbed HC can be suppressed better and the absorbed HC can be held up to a higher temperature.

It is desirable that the silica/alumina ratio of the zeolite should be determined to be within the range of 20

25   to 1500, and particularly within the range of 20 to 300. In that case, high heat resistance can be ensured, without impairing the HC absorbing capacity but keeping the absorbing capacity high.

It is desirable that the silica/alumina ratio of the

30   zeolite should be determined so that breaks are not produced in the structure of the zeolite at 900°C. In that case, the structure of the zeolite does not easily break, and hence the durability of the zeolite catalyst improves.

It is desirable that the zeolite should be arranged on a support, where the amount of the zeolite supported should be determined to be within the range of 90g/L to 130g/L. In that case, a sufficient amount of absorption can be ensured, and hence the HC removal performance can be improved.

It is desirable that the zeolite should contain one or more elements chosen from among Ag, Mn, Fe, Ni and Cu. In that case, the temperature at which the desorption of HC from the absorbent starts can be made higher.

It is desirable that the absorbent should be arranged on a support and a three-way catalyst should be arranged on a downstream-side part of the support. In that case, the HC desorbed from the absorbent can be converted by the three-way catalyst arranged downstream.

It is desirable that the absorbent should be arranged on a support and a three-way catalyst layer should be formed on the absorbent. In that case, the HC desorbed can be removed with certainty.

Preferably, the three-way catalyst layer contains Ce. In that case, due to the oxygen storage function (O_2 storage function) of Ce, HC can be removed by oxidation in good manner even when the three-way catalyst layer is in a reducing atmosphere containing a large amount of HC and CO.

It is desirable that the amount of the zeolite arranged on the support should be determined so that the zeolite supported has a capacity to absorb a larger amount of HC than the total amount of HC discharged from the internal combustion engine from the time when the internal combustion engine is cold-started until the three-way catalyst layer becomes activated. In that case, the emission of HC at the time of cold start can be reduced with certainty.

It is desirable that an upstream-side three-way catalyst should be arranged upstream of said support. In that case, since HC is converted by the upstream-side three-way catalyst even though in a small amount, the amount of HC contained in exhaust gas downstream of the upstream-side three-way catalyst is reduced. Thus, the amount of HC to be absorbed in the absorbent can be reduced.

It is desirable that the upstream-side three-way catalyst should be arranged on a support formed to have a cell density higher than the cell density of said support. In that case, the upstream-side three-way catalyst warming speed can be increased, so that HC can be converted efficiently.

It is desirable that the amount of the zeolite arranged on the support should be determined so that the zeolite supported has a capacity to absorb a larger amount of HC than the total amount of HC discharged from the engine from the time when the engine is cold-started until the upstream-side three-way catalyst becomes activated. In that case, the emission of the HC discharged from the engine to the outside until the upstream-side three-way catalyst becomes activated can be reduced.

It is desirable that the absorbent should have the HC desorbing capacity which becomes greatest at a temperature of 160°C or higher. In that case, the HC removal rate can be improved.

As a more desirable aspect, it is desirable that an absorbent comprising CON type zeolite should be arranged in an exhaust passage of an internal combustion engine. Desirably, the CON type zeolite is SSZ-26 or SSZ-33 having a three-dimensional structure in which series of stacked rings intersect each other. In that case, compared with the case using conventional β type zeolite, the desorption

of the absorbed HC can be suppressed better and the absorbed HC can be held up to a higher temperature.

Brief Description of the Drawings

5   FIG. 1 is a diagram schematically showing the structure of an exhaust gas cleaning-up device according to this invention;

FIG. 2 is a cross-sectional view showing how a three-way catalyst layer and an HC absorption layer are formed in

10   an UCC;

FIG. 3 is a diagram schematically showing the crystal structure of CON type zeolite;

FIG. 4 is a diagram showing relation between the amount of HC absorbed in CON type zeolite and the amount of

15   HC emitted when temperature changes,

FIG. 5 is a diagram schematically showing the structure of an exhaust gas cleaning-up device in another embodiment in which the support of an UCC is divided into a preceding-stage part and a succeeding-stage part,

20   FIG. 6 shows relation between temperature and HC emission (HC desorption) from the UCC, obtained in a test where a new UCC was fit to an engine;

FIG. 7 shows the same test result as FIG. 6 in the form of a bar graph showing HC emission in different

25   temperature ranges;

FIG. 8 shows the result of a test where an UCC subjected to a heat test was used,

FIG. 9 is a diagram showing relation between the Si/Al ratio of CON type zeolite and the rate of reduction of NMHC

30   emission;

FIG. 10 is a diagram showing relation between the amount of CON type zeolite and the rate of reduction of NMHC emission; and

FIG. 11 is a diagram showing how the HC desorption temperature changes when CON zeolite supports a transition metal.

5 **Best Mode of Carrying out the Invention**

Referring to the drawings, embodiments of this invention will be described.

FIG. 1 is a diagram schematically showing the structure of an exhaust gas cleaning-up device in an

10 embodiment of this invention. FIG. 2 is a cross-sectional view showing how a three-way catalyst layer and an HC absorption layer are formed in an catalytic converter provided in the exhaust gas cleaning-up device.

As shown in FIG. 1, the exhaust gas cleaning-up device

15 in an embodiment of this invention includes an MCC (manifold catalytic converter) 10 arranged in an upstream section (in this example, formed by an exhaust manifold) 31a of an exhaust passage 31 connected to an engine body (hereinafter referred to simply as "engine") 30, and an UCC

20 (under-floor catalytic converter) 20 arranged in a downstream section 31b of the exhaust passage 31.

The MCC 10 is formed as a three-way catalytic converter.

Within a catalyst case of the UCC 20, a support with a

25 large number of cell holes is provided, and a palladium/rhodium (Pd/Rh) three-way catalyst and an HC absorbent comprising CON type zeolite comprising silica (Si) and alumina (Al) as major constituents and capable of absorbing HC contained in exhaust gas are arranged on the

30 support.

Specifically, as shown in FIG. 2, the HC absorbent is arranged to form an HC absorption layer 2 covering the inner surface of each cell hole 3a in the support 3, and

the three-way catalyst is arranged to form a three-way catalyst layer 1 over the surface of the HC absorption layer 2.

FIG. 3 schematically shows the crystal structure of CON type zeolite.

CON type zeolite has a three-dimensional structure in which series of stacked rings consisting of a specific number of members intersect series of stacked rings consisting of a different specific number of members so that the crystal has two types of pores different in diameter (pores formed by series of stacked 10-membered rings (referred to as "10-membered ring pores" and pores formed by series of stacked 12-membered rings (referred to as "12-membered ring pores")).

Further, in the crystal of CON type zeolite, the faces of unit crystals form the three-dimensional pores, where the axes of stacked adjacent rings consisting of the same number of members are out of alignment.

Due to these structural features, CON type zeolite has a characteristic that HC easily comes into the crystal through the 12-membered ring pores. HC comes into the crystal also through the 10-membered ring pores, but more slowly than through the 12-membered ring pores. Hence, CON type zeolite has also a characteristic that HC passes through the 10-membered ring pores slowly.

CON type zeolite has further a characteristic that even when the temperature rises, HC is not easily desorbed from the crystal, since the HC that has once come deeply into the crystal does not easily pass through the crystal due to the complicated arrangement of pore passages due to the non-aligned arrangement of axes of stacked adjacent rings consisting of the same number of members, and HC only slowly passes through the crystal in a direction

corresponding to one of the three dimensions of the crystal through the 10-membered ring pores, because of their small diameter.

Thus, CON type zeolite has a characteristic that the 12-membered ring pores with a large diameter promote the absorption of HC and the 10-membered ring pores with a small diameter suppress the desorption of HC at high temperatures.

Further, HC has a property that it easily attaches to Al, which is one of the two major constituents Si and Al of zeolite. It was confirmed through an experiment that also in the case of CON type zeolite, a larger proportion of Al, or in other words, a smaller Si/Al ratio between Si in the form of silica and Al in the form of alumina improves the absorbing capacity of the HC absorption layer 2.

Zeolite has, however, also a characteristic that when the proportion of Al is larger, namely the Si/Al ratio is smaller, the bond of Al in the structure is more easily broken at high temperatures, and hence, the structure more easily breaks.

However, through an experiment, it was confirmed that in the case of CON type zeolite, even when the Si/Al ratio is small, zeolite exposed to high-temperature exhaust gas does not show a structure broken to a large extent, and that the HC absorption layer 2 has a higher absorbing capacity and desorption suppressing capacity at high temperatures, compared with when the HC absorption layer is formed of a conventionally-used zeolite.

Thus, in the present embodiment, the Si/Al ratio of CON type zeolite is determined to be within a range which ensures that even at a high temperature (900°C, for example) of exhaust gas, the structure of zeolite shows few breaks of Al bond and that the HC absorption layer 2 has a

high absorbing capacity. Compared with β type zeolite, etc., CON type zeolite has a higher HC absorbing capacity, and has higher heat resistance and better durability even when the Si/Al ratio is smaller. According to an

5   experiment described later, in the case of CON type zeolite, it is desirable that the Si/Al ratio should be determined to be within a range of about 20 to 1500. Particularly when the Si/Al ratio is determined to be within a range of about 20 to 300, it is possible to keep the absorbing

10   capacity high and ensure sufficient heat resistance without impairing the HC desorbing capacity.

The amount of HC absorbed is proportional to the amount of zeolite. Hence, when the amount of zeolite is smaller, the HC desorption speed, namely the speed with

15   which HC is desorbed is higher. Meanwhile, when the amount of zeolite is larger, the HC desorption speed is lower, however, the larger amount of zeolite increases the thermal capacity and hence tends to reduce a rise in temperature.

It is also known that the HC desorption speed is

20   inversely related to the amount of HC absorbed. Specifically, the maximum HC absorption amount is determined by the amount of zeolite, and, as shown in FIG. 4, when the ratio of the amount of HC absorbed in zeolite to the maximum HC absorption amount in zeolite (referred to

25   as "absorption ratio") is greater, the amount of HC desorbed at low temperatures is greater. Meanwhile, the absorption ratio is smaller, the desorption of absorbed HC can be suppressed up to higher temperatures. Through an experiment, it was confirmed that also CON type zeolite has

30   the same characteristic.

Hence, in the present embodiment, while the Si/Al ratio is optimized, the amount of CON type zeolite is determined within such a range that keeps the thermal

capacity within an allowable range. Further, the amount of CON type zeolite is determined to have a capacity to absorb a larger amount of HC than the total amount of HC discharged from the time when the engine 30 is cold until

5 the MMC 10 becomes activated. According to an experiment, it is desirable that the amount of CON type zeolite contained in the HC absorption layer 2 should be in the range of about 90g/L to 130g/L, in which case a sufficient HC absorption amount can be ensured.

10 The chemical absorption characteristic of zeolite is such that the absorption of unsaturated hydrocarbon such as olefin is dominant. Hence, if Pd which is especially effective in oxidation of olefin is used as a noble metal constituting the three-way catalyst layer 1, it tends to

15 promote the absorption and desorption by oxidation of HC. Through an experiment, it was confirmed that also CON zeolite shows the same characteristic.

Hence, in the present embodiment, paradium (Pd) and rhodium (Rh) are used as noble metals constituting the

20 three-way catalyst layer 1.

Further, when the cell-hole 3a density of the support 3 of the UCC 20 is higher, the surface area of the HC absorption layer 2 becomes greater, which means that a greater amount of the absorbent, and therefore of zeolite

25 is arranged on the support. Accordingly, HC is more easily absorbed. This was confirmed also with respect to CON type zeolite, through an experiment.

Thus, in the present embodiment, the cell density of the support of the UCC 20 is optimized in the light of the

30 total amount of the absorbent (zeolite).

The cell density of the support of the MCC 10 arranged in the upstream section of the exhaust passage is determined to be higher than the cell density of the

support of the UCC 20. When the cell density is higher, the area of the surface of the three-way catalyst in contact with exhaust gas discharged from the engine 30 becomes larger, so that a larger amount of HC discharged

5 from the engine is oxidized, so that a rise in temperature due to the reaction heat becomes greater. Further, if the wall of the support is made thinner to increase the cell density, the thinner wall thickness reduces the heat mass. Consequently, the warming characteristic of the MCC 10

10 improves, so that the time taken for activation becomes shorter, so that the amount of HC discharged when the engine 30 is cold-started is reduced. Consequently, the total amount of HC to be absorbed in the HC absorption layer 2 of the UCC 20 is reduced. Accordingly, HC is more

15 easily absorbed in the HC absorption layer 2, and the capacity of the UCC 20 can be reduced.

As shown in FIG. 5, in an alternative embodiment, the support 3 of the UCC 20 is divided into an upstream part and a downstream part, and an HC absorption layer 2 and a

20 three-way catalyst layer 1 are formed on them, respectively. In this case, if the cell density of the upstream part is made high and the cell density of the downstream part is made low, HC tends to be more easily absorbed in the HC absorption layer 2. Through an experiment, the same

25 characteristic was confirmed also with respect to CON type zeolite. Hence, when the support 3 of the UCC 20 is divided into an upstream part and a downstream part, it is desirable that the cell density of the upstream part should be made high and the cell density of the downstream part

30 should be made low, and that an HC absorption layer 2 and a three-way catalyst layer 1 should be formed on the upstream part and the downstream part, respectively.

In the exhaust gas cleaning-up device described above,

when the engine 30 is cold, exhaust gas is cleaned up chiefly by the MCC 10 located upstream, which is warmed by the exhaust gas in early time. The HC in the exhaust gas which is not converted in the MCC 10 is absorbed in the HC

5   absorption layer 20 of the UCC 20. Then, as the engine 30 warms so that the MCC 10 warms so that the three-way catalytic function of the MCC 10 becomes activated, the exhaust gas is cleaned up by the MCC 10. Here, since the high-temperature exhaust gas warms the MCC 10 at a high

10   speed, the three-way catalytic function of the MCC 10 becomes activated in early time. When the upstream MCC 10 converts HC even though in a small amount, the HC contained in the exhaust gas downstream of the MCC 10 is reduced. Thus, the amount of HC to be absorbed in the HC absorption

15   layer 2 of the UCC 20 can be reduced.

As mentioned above, in the UCC 20, the amount of zeolite is determined to have a capacity to absorb a larger amount of HC than the total amount of HC discharged from the time when the engine 30 is cold until the MMC 10

20   becomes activated. Hence, afterwards, when the UCC 20 warms and becomes activated, the desorption of HC from the HC absorption layer 2 of the UCC 20 starts, however, the HC desorbed from the absorption layer 2 is converted by the three-way catalyst layer 1 which, as well as the HC

25   absorption layer 2, has warmed and become activated. Thus, it is possible to reduce the capacity of the HC absorption layer 2 and still reduce, to a large degree, the amount of HC contained in the exhaust gas emitted to the outside when the engine is cold.

30   In this exhaust gas cleaning-up device, since the high-temperature exhaust gas warms the MCC 10 at a high speed, the three-way catalytic function of the MCC 10 becomes activated in early time. Hence, the time between

the HC absorption layer 2 of the UCC 20 starting the absorption of HC and the MCC 10 warming to a temperature at which the MCC 10 can convert HC (activation temperature) can be made very short. Further, the HC which is not

5   converted in the MCC 10 when the MCC 10 is cold can be absorbed in the HC absorption layer 2 of the UCC 20, and the HC desorbed from the HC absorption layer 2 after the UCC 20 becomes activated can be converted by the three-way catalyst layer 1 in good manner. Thus, the amount of HC

10   not converted in the MCC 10 and emitted to the outside can be reduced to a great degree.

In order to activate the MCC 10 further earlier, the ignition timing may be retarded in the engine 30 to warm the exhaust. Further, when the engine 30 is a direct-

15   ignition engine, carrying out additional injection (sub-injection) of fuel in the expansion stoke is effective to warm the exhaust.

In the above, the case using CON type zeolite having pores formed by 10-membered rings and pores formed by 12-

20   membered rings has been described. It is however possible to use CON type zeolite having pores formed by 10-membered rings and pores formed by rings consisting of more than 12 members, or a zeolite having three or more types of pores formed by rings different in the number of members.

25   [Examples]

Specific examples of the exhaust gas cleaning-up device according to the present invention arranged as described above will be described below.

First, how to form the three-way catalyst layer and HC

30   absorption layer of the UCC will be described.

(1) Formation of the HC absorption layer

A slurry for forming an HC absorption layer was prepared by mixing, in a ball mill, a 50 wt% aqueous

dispersion in which CON type zeolite (product name: SSZ-33 or SSZ-26 made by Chevron) as an absorbent and SiO_2 in the amount of 10 wt% of the absorbent in the form of SiO_2 sol were dispersed in water.

5   Then, the slurry was applied onto a honeycomb body of cordierite (1L) according to an intended weight, then dried and then baked in air at 500°C, so that an HC absoption layer was formed.

(2)   Formation of the three-way catalyst layer

10   A slurry containing 50 wt% of solids was prepared by grinding and mixing salts of noble metals selected and γ-alumina in a ball mill.

      Then, the slurry was applied onto the cordierite honeycomb body coated with the HC absorption layer

15   according to an intended weight, then dried and then baked in air at 500°C as in the case of the HC absorption layer, so that a three-way catalyst layer was formed.

(3)   Heating

      After the HC absorption layer and three-way catalyst

20   layer were formed, heating was preformed in an engine in an atmosphere of a lean air/fuel ratio (A/F = 23) and an atmosphere of a rich air/fuel ratio (A/F = 13) at the catalyst center temperature 950°C for 40 hours.

      Next, the evaluation of absorbent catalytic converters

25   having a three-way catalyst layer and an HC absorption layer formed as described above will be described.

      First, only in respect of the HC absorption layer, the HC desorption temperature when CON type zeolite was used and the HC desorption temperature when β type zeolite was

30   used were compared. It is to be noted that zeolite was used in powder form, and that toluene was used as to-be-absorbed HC.

      FIG. 6 is a graph showing HC emission (HC desorption)

in a TPD (temperature programmed desorption) test conducted using new zeolite, where the case using CON type zeolite and the case using β type zeolite are compared. FIG. 7 shows the same test result in the form of a bar graph

5 showing HC emission in different temperature ranges.

As seen from FIGS. 6 and 7, compared with the case in which β type zeolite is used (broken line), when CON type zeolite is used for the HC absorption layer (solid line), the HC desorption reduces in a low temperature range and

10 dramatically increases in a high temperature range. The HC desorption is great particularly in the range of 160°C and higher, and reaches the peak at a temperature close to 200°C. This means that, compared with the case in which β type zeolite is used, when CON type zeolite is used, a

15 greater amount of HC is held within the HC absorption layer until the temperature exceeds the lowest activation temperature for the three-way catalyst layer (about 200°C), and that the HC held is desorbed after the temperature exceeds the lowest activation temperature.

20 As stated above, CON type zeolite has a pored three-dimensional structure, where the unit crystal contains pores of two different types, namely, a pore of a small diameter formed by 10-membered rings and a pore of a large diameter formed by 12-membered rings. Because of this

25 structure, CON type zeolite has a characteristic that the large-diameter pores formed by 12-membered rings promote the absorption of HC, while the small-diameter pores formed by 10-membered rings suppress the desorption of HC. The above test result verified that it is possible to absorb

30 and hold a large proportion of HC contained in exhaust gas within the HC absorption layer until the three-way catalyst layer warms to above the lowest activation temperature (about 200°C) and desorb it after the three-way catalyst

layer warms to above the lowest activation temperature, and hence verified that the use of CON type zeolite for the HC absorption layer of the absorbent catalytic converter is very effective to improve the HC removal 1performance.

5   FIG. 8 shows, in the same way as in FIG. 6, HC emission in a TPD test conducted using zeolite subjected, in advance, to a heat test in which zeolite was held at 800°C in 10% vapor for 5 hours. As seen from this graph, even under the condition that zeolite is subjected to the

10   heat test in advance, in the temperature range exceeding the lowest activation temperature (about 200°C) for the three-way catalyst layer, the HC desorption is far greater when CON type zeolite is used for the HC absorption layer than when β type zeolite is used, although the capacity of

15   CON type zeolite subjected to the heat test is lower than that of new CON type zeolite. By this, it was verified that the absorbent catalytic converter using CON type zeolite for the HC absorption layer is sufficiently suitable for practical use.

20   Further, in respect of the rate of reduction of NMHC (non methane hydro carbon) emission after the UCC (HC removal rate in the whole exhaust system), comparative evaluation was performed on the UCC 20 using CON type zeolite for the HC absorption layer, where the Si/Al ratio

25   of CON type zeolite, the amount of CON type zeolite, the noble metals used for the three-way catalyst layer, the form of the support (one body or divided into two parts), and the cell density of the support were changed.

          The MCC 10 used here was one using a catalyst

30   containing palladium (Pd) and rhodium (Rh) as major constituents, and formed with a support capacity 0.7L, a support cell density 2 mil/900 cell, and a Pd/Rh ratio 2.1/0.3[g/L].

Further, in order to achieve early activation of the MCC 10, warming control by retarding the ignition timing was performed in parallel.

Table 1 shows the result of a test about the rate of
5   reduction of NMHC emission in the cold state immediately after the start of the engine, where the Si/Al ratio of CON type zeolite in the UCC 20 was changed. Further, FIG. 9 shows the relation between the Si/Al ratio of CON type zeolite and the rate of reduction of NMHC emission based on
10   this test result.

[Table 1]

		UCC			Rate of
Support (Cell density)	Capac-ity	Three-way catalyst layer	HC absorption layer		reduction of NMHC
		Noble metals	Si/Al	Amount	emission
4.3mil/600cell	1L	Pd/Rh=3/0.3	20	100g/L	75
ditto	ditto	ditto	100	ditto	80
ditto	ditto	ditto	1000	ditto	80
ditto	ditto	ditto	2000	ditto	50

Table 1 and FIG. 9 show that in the UCC using CON type zeolite, when the Si/Al ratio of CON type zeolite is in the range of 100 to 1000, the rate of reduction of NMHC
15   emission is about 80%, which is highest, and that when the Si/Al ratio of CON type zeolite is in the range of about 20 to 1500, the HC removal rate can be kept high. Particularly by determining the Si/Al ratio to be within the range of 20 to 300, it is possible to increase the rate
20   of reduction of HC emission, while keeping the HC absorption amount and the heat resistance high.

Table 2 shows the result of a test about the rate of reduction of NMHC emission, where CON type zeolite of Si/Al

ratio 100 was used for the UCC 20 and the amount of CON type zeolite was changed. Further, FIG. 10 shows the relation between the amount of CON type zeolite and the rate of reduction of NMHC emission based on this test result.

[Table 2]

		UCC			Rate of
Support (cell density)	Capac- ity	Three-way catalyst layer	HC absorption layer		reduction of NMHC
		Noble metals	Si/Al	Amount	emission
4.3mil/600cell	ditto	Pd/Rh=3/0.3	100	50g/L	60
ditto	ditto	ditto	ditto	100g/L	80
ditto	ditto	ditto	ditto	150g/L	75

Table 2 and FIG. 10 show that in the UCC 20 using CON type zeolite, when the amount of CON type zeolite is 100g/L, the rate of reduction of NMHC emission is about 80%, which is highest, and that when the amount of CON type zeolite is in the range of about 90g/L to 130g/L, the HC removal rate can be kept high. Hence, the amount of CON type zeolite is determined to be within the range of about 90 g/L to 130 g/L.

Table 3 shows the result of a test about the rate of reduction of NMHC emission, where 100g/L of CON type zeolite was used for the UCC 20, and palladium and rhodium (Pd/Rh) or platinum and rhodium (Pt/Rh) were used as major noble metals constituting the three-way catalyst layer. It is noted that the ratio of Pd to Rh is different from the ratio of Pt to Pd, each ratio being a typical ratio for forming an optimal three-way catalyst layer using Pd or Pt.

[Table 3]

		UCC				Rate of
Support (cell desntiy)	Capac-ity	Three-way catalyst layer	HC absorption layer			reduction of NMHC
		Noble metals	Si/Al	Amount		emission
4.3mil/600cell	1L	Pd/Rh=3/0.3	100	100g/L		80
ditto	ditto	Pt/Rh=2.5/0.5	ditto	ditto		70

Table 3 shows that in the UCC 20 using CON type
zeolite, the rate of reduction of NMHC emission is higher
when Pd and Rh are major noble metals constituting the
three-way catalyst layer than when Pt and Rh are. The
reason for this is thought to be as follows: As mentioned
above, the chemical absorption characteristic of zeolite is
such that the absorption of unsaturated hydrocarbon such as
olefin is dominant, and therefore Pd which is especially
effective in oxidation of olefin contributes much to
absorption and desorption by oxidation of HC. Thus, the
three-way catalyst layer is formed using Pd and Rh as major
noble metals.

Table 4 shows the result of a test about the rate of
reduction of NMHC emission, where a support in one body or
a support divided into two parts was used, and the cell
density of the support was changed. Specifically, as shown
in table 4, a support in example ① was of capacity 1L and
cell density 4.3mil/600cell, a support in example ② was of
capacity 1L and cell density 2.5mil/900cell, a support in
example ③ was, as shown in FIG. 5, divided into a
preceding-stage part of 0.4L and a succeeding-stage part of
0.6L, each with a cell density of 4.3mil/600cell, a support
in example ④ was divided into a preceding-stage part of
0.4L and a succeeding-stage part of 0.6L, each with a cell

density of 2.5mil/900cell, a support in the example ⑤ was
divided into a preceding-stage part of capacity 0.4L and
cell density 2.5mil/900cell and a succeeding-stage part of
capacity 0.6L and cell density 4.3mil/600cell, and a
5   support in the example ⑥ was divided into a preceding-
stage part of capacity 0.4L and cell density 4.3mil/600cell
and a succeeding-stage part of capacity 0.6L and cell
density 2.5mil/900cell.

[Table 4]

	Support (cell density)	Capac-ity	UCC			Rate of reduction of NMHC emission
			Three-way catalyst layer	HC absorption layer		
			Noble metals	Si/Al	Amount	
①	4.3mil/600cell	1L	Pd/Rh=3/0.3	100	100g/L	80
②	2.5mil/900cell	ditto	ditto	ditto	ditto	85
③	4.3mil/600cell	0.4L 0.6L	ditto	ditto	ditto	82
④	2.5mil/900cell	0.4L 0.6L	ditto	ditto	ditto	85
⑤	2.5mil/900cell 4.3mil/600cell	0.4L 0.6L	ditto	ditto	ditto	86
⑥	4.3mil/600cell 2.5mil/900cell	0.4L 0.6L	ditto	ditto	ditto	80

10   In Table 4, comparison between examples ① and ② shows
that, in the UCC 20 using CON type zeolite, the rate of
reduction of NMHC emission is higher when the cell density
of the support is 2.5mil/900cell (higher cell density) than
when it is 4.3mil/600cell (lower cell density). The reason
15   for this is thought to be that when the cell density is

higher, the surface area of the HC absorption layer is greater so that HC is more easily absorbed. Thus, when the support is not divided but provided in one body, the support is formed to have a high cell density.

5   Comparison between examples ③ and ④ shows that the rate of reduction of NMHC emission is higher when the preceding-stage part and succeeding-stage part of the support are both formed with a cell density 2.5mil/900cell than when they are both formed with a cell density

10   4.3mil/600cell.

Further, comparison between examples ⑤ and ⑥ shows that the rate of reduction of NMHC emission is higher when the preceding-stage part and succeeding stage part of the support are formed with cell densities 2.5mil/900cell and

15   4.3mil/600cell, respectively, than when they are formed with cell densities 4.3mil/600cell and 2.5mil/900cell, respectively.

Hence, when the support is divided into a preceding-stage part and a succeeding-stage part, it is arranged that

20   the preceding-stage part has a higher cell density than the succeeding-stage part.

As understood from the above, by adopting CON type zeolite (product name: SSZ-33 made by Chevron) as an HC absorbent for the UCC and optimizing the UCC, it is

25   possible to keep the HC removal rate high.

In the above, embodiments of the present invention have been described referring to specific examples. The present invention is however not limited to the described embodiments.

30   For example, in the above-described embodiments, a three-way catalyst is used in the MCC 10. This is to reduce the amount of HC to be absorbed and thereby increase the efficiency of oxidation of HC desorbed. The similar

effect is produced when the MCC 10 is formed to have a three-way catalyst layer 1 and an HC absorption layer 2 on a support, like the UCC 20.

Further, for the three-way catalyst layer 1 of the MCC 10 or the UCC 20, nickel (Ni) can be added. Among the transition metals, Ni is particularly high in the capacity to absorb and oxidize CO. Hence, when the three-way catalyst layer 1 contains Ni, an adequate amount of CO is oxidized at the three-way catalyst layer 1, so that the three-way catalyst layer 1 warms and becomes activated in earlier time.

Further, when it is arranged that zeolite supports a transition metal such as Ag, Fe, Ci, Cu or the like, chemical absorbing power acts between the transition metal and HC, which makes the desorption temperature higher, as shown in FIG. 11.

Further, also ceria (Ce) can be added for the three-way catalyst layer 1 of the UCC 20. Since Ce has an oxygen storage capacity (O_2 storage capacity), HC can be removed in good manner by oxidation with the stored O_2, even when the three-way catalyst layer 1 is in a reducing atmosphere containing a large amount of HC and CO. Consequently, the HC removal performance is further improved.